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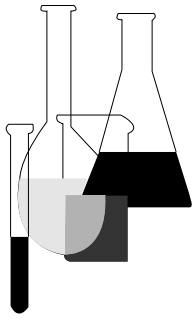
Occupational and Residential Exposure Test Guidelines

OPPTS 875.2200
Soil Residue Dissipation



INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

This guideline, along with the others in Series 875.2000 through 875.2900, is being substantially revised for publication in 1997. However, the current guidelines are still official. Before initiating any studies for post-application exposure registrants should contact EPA's Occupational and Residential Exposure Branch (within the Office of Pesticide Programs) at 703–305–6094.

Final Guideline Release: This guideline is available from the U.S. Government Printing Office, Washington, DC 20402 on *The Federal Bulletin Board*. By modem dial 202–512–1387, telnet and ftp: fedbbs.access.gpo.gov (IP 162.140.64.19), internet: http://fedbbs.access.gpo.gov, or call 202–512–0132 for disks or paper copies. This guideline is also available electronically in ASCII and PDF (portable document format) from the EPA Public Access Gopher (gopher.epa.gov) under the heading ''Environmental Test Methods and Guidelines.''

OPPTS 875.2200 Soil residue dissipation.

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*).

(2) **Background.** The source material used in developing this harmonized OPPTS test guideline is OPP guideline 132. This guideline should be used with OPPTS 875.2000 and 875.2900.

(b) **Purpose.** Requirements of 40 CFR 158.390 and described in this guideline are confined to the measurements of pesticide residues which are deposited on and remain on surfaces after pesticide application. These surfaces are limited to those that can be touched or disturbed by people, and from which residues can be dislodged during the performance of various tasks and subsequently deposited on human skin and clothing or inhaled.

(c) **Test standards—**(1) **Test substance.** A typical end-use product should be used for this study.

(2) **Sites for conduct of tests.** Since climate strongly influences the dissipation of pesticide residues, the applicant should perform dissipation study at a site representative of the climatic conditions expected in the intended use areas. The Agency will provide guidance on the choice of site upon request.

(3) **Substitutions for sites.** In certain cases, data from one site (when available) may be substituted for data from another site when surface characteristics are generally similar or nearly identical (e.g., orange and grapefruit orchard applications). For those cases, available residue data should demonstrate that dissipation rates at the two sites do not differ significantly for similar use patterns.

(4) **Method of application.** The test substance should be applied by application methods recommended for the end-use product. Application of the test substance to the site, area, or objects should be at the least dilution and highest rate permitted for that end-use product.

(5) **Timing of application.** The test substance should be applied at the time of year or season that would normally be recommended to achieve satisfactory pest control by the product.

(6) **Meteorological conditions.** Daily meteorological conditions at or near the site of application should be recorded as part of the data in this study. Such data would include, as appropriate, temperature, wind speed, daily rainfall, humidity, and similar information.

(7) **Standards for sample collection—**(i) **Duplicate samples.** Duplicate foliar samples should be collected periodically for the development of dissipation curves. The first samples should be taken as soon as the

spray has dried or the dust has settled. The intervals at the start of sampling should be relatively short and may increase with time. For example, samples taken as soon as the spray has dried or the dust has settled, and at 1, 2, 5, 7, 14, 21, 28, and 35 days after pesticide application would probably be appropriate for some pesticides. Comparable control or baseline samples should be collected immediately before the pesticide application. If analyses of samples reveal dislodgeable residues above the reentry level, sampling and analyses should continue until a level at or below the reentry level is reached.

(ii) **Additional standards for soil samples.** (A) Whenever the applied pesticide deposits on, is incorporated into, or diffuses into soil at the site of application and whenever tasks at the treated site will involve exposure of workers to large amounts of soil, duplicate soil samples for pesticide residue analysis should be collected from the soil surface or from not more than the upper 1 cm of soil in the test plot.

(B) The fine material should be isolated from the soil samples without grinding to give all of the material having particle sizes of 147 μm or less without particles larger than 147 μm. The fine material will be extracted for residue analysis.

(iii) **Sample storage.** Samples and sample extracts may be stored for later analysis only if fortified controls are included to permit evaluation of possible residue deterioration during storage. Such samples should be stored under conditions which will minimize deterioration.

(8) **Procedures for chemical extraction and analysis.** The dislodgeable pesticide residues should be extracted from the foliar material and soil, isolated from interfering materials by suitable cleanup procedures, and quantified.

(d) **Reporting of test results.** (1) In addition to meeting the general reporting requirements of 40 CFR 158.390 the test report should also meet the following requirements: For residues on soil, the analytical results should be expressed in terms of micrograms per gram of fine material. The fine material should be reported in milligrams or micrograms per square centimeter of surface of the soil area from which the sample was obtained. Soil and water methods should identify and quantify the total toxic residue, including the parent compound, toxicologically significant metabolites and degradates. This guideline does not include those environmental chemistry methods from studies that use radioactive isotopes.

(2) These methods may be validated in an EPA laboratory to determine if they identify and quantify the pesticide parent compound, toxicologically significant metabolitess and degradates at the level indicated. The results from the soil and water method validation program may be used to support regulatory decisions regarding the reliability and validity of the chemistry data sent to the Agency with exposure, environmental

fate, and ecological effects studies. Registrants should immediately send 5 gm of the active ingredient analytical grade standard and 1 gm, or a reasonable amount, of any toxicologically significant metabolites and degradates to the EPA repository at Research Triangle Park, North Carolina. Registrants shall also send 1 gm, or a reasonable amount, of any stable derivative that is used to identify and quantitate the target analytes to the EPA repository. All environmental chemistry methods should be stamped nonconfidential.

(3) Registrants must provide EPA with accurate and precise data on the performance of those soil and water chemistry methods that are used to develop laboratory and/or field residue data to support exposure, environmental fate, and ecological effects studies for registration and reregistration. This includes all single or multianalyte methods for the parent compounds, toxicologically significant metabolites, and degradates in each environmental matrix.

(4) Registrants shall provide EPA with clearly written and complete analytical methods that describe the exact procedure, materials, and equipment to be used by regulatory chemists to validate their methods. Analytical methods shall be practical, rapid, and quantitate analytes of interest. The Agency will accept best available methods for those parent compounds, toxicologically significant metabolites, and degradates that have significant risks and require state-of-the-art equipment to measure trace amounts of analytes. Both practical and rapid and best available methods must use equipment that is commercially available in the United States. If methods use conventional gas chromatography, liquid chromatography, etc., registrants shall submit confirmatory methods using GC/MS, LC/MS, second column or other suitable procedures. Well established confirmatory methods that are used to generate study data do not require another confirmatory procedure.

(5) Regulatory chemists should be able to validate practical and rapid analytical methods using a standard set of samples in 24 hours (e.g., three 8–h working days); however, EPA recognizes that best available methods may require additional time. Each set should have an appropriate number of samples with quality control samples intermingled. EPA regulatory chemists should be able to quickly validate soil and water methods for each test level and matrix.

(6) Registrants shall submit performance data to EPA demonstrating that an adequate number of samples for each test level were extracted, cleaned up, and analyzed. This data should support the established limit of quantitation (LOQs) and precision and accuracy for each method. Target levels for the mean recoveries should be distributed between 70 and 120 percent of the known quantity of the pesticide/ metabolite spiked into the matrix blanks at the LOQ or above during the method validation, but registrants should report individual values for recoveries and standard devi-

ations for known quantities of pesticides and metabolites in fortified samples at each spiking level.

(7) The relative standard deviation (RSD) of replicate measurements of recoveries should not exceed the target level of 20 percent at the LOQ or above in any set. EPA recognizes that some methods may not be able to meet these precision requirements. The LOQ may be determined as described in paragraph (g)(4) of this guideline. If they are determined in any other way, registrants shall identify the source of that information and provide EPA with a clearly written explanation of how they calculated those values.

(8) Registrants shall not correct sample values for recoveries. Registrants shall also describe any matrix or solvent effects that result in signal enhancement, masking or suppression and the impact those effects have on the test results.

(9) Registrants shall clearly identify those laboratories that developed the data for the soil and water methods they submit to EPA. Registrants shall use an independent laboratory to validate soil and water methods that are used to support appropriate exposure, environmental fate and ecological effects studies. Methods will not be rejected outright for failure to comply with each and every aspect of this guideline but will be reviewed on a case-by-case basis to determine their suitability by chemists at OPP's Analytical Chemistry Laboratories.

(e) **Evaluation and use of data.** Data obtained from this study are for the development of dissipation curves which can be used in the calculation of reentry intervals according to the approaches described in OPPTS 875.2900.

(f) **Data report**—(1) **Information to be reported to the Agency.** The following information should be submitted by registrants:

(i) Name, address, telephone number of the study director and lead chemist for the laboratory that developed the method and the laboratory that validated the analytical methods.

(ii) Detailed stepwise description of the analytical methods developed for each environmental matrix.

(iii) An example of sample calculations and an explanation of how the LOQ was determined.

(iv) Precision and accuracy data, including recoveries, control charts, and other performance data for each method,

(v) Representative chromatograms/spectra for each analyte measured in each matrix and at all spiking levels, including method and matrix blanks. Copies of the chromatograms/spectra are also required for the

standards that were used to quantitate the analytes in the representative matrix chromatograms/ spectra submitted to EPA.

(vi) Description of the supplies, materials, and instruments used for each method (these must be commercially available in the United States).

(vii) Description of any problems encountered with each method and any steps considered critical, i.e. steps where little variation is allowed and where directions must be followed precisely.

(viii) The number of worker–hours required to extract, cleanup, and analyze one set of samples.

(ix) Registrants or their representative shall keep 10 lb, or a reasonable amount, of each type of blank soil tested until the product has been registered with EPA. This soil will be available to EPA on request.

(x) A statement of adherence to the FIFRA Good Laboratory Practices Standards (GLP), which should be used to support both the ecological effects, exposure, environmental fate study data, and the validation data that demonstrate the performance of each soil and water method. This information should be sent to EPA/OPP Registration Division and a complete hard copy with a computer floppy disc that can be used on a personal computer with Word Perfect 5.1 or newer should be sent to: Environmental Protection Agency Environmental Chemistry Section Building 1105 Stennis Space Center, Mississippi 39529–6000 ATTN: Lab Chief.

(2) **Evaluation of the environmental chemistry methods sent to EPA.** (i) EPA plans to evaluate a certain number of the written soil and water methods that are used by registrants to support appropriate ecological effects, exposure, and environmental fate studies.

(ii) The first phase involves an evaluation of the written soil or water method and data sent to EPA by registrants. During this phase an EPA chemist will determine if the written method and data meet all of the requirements described in this guideline. That evaluation will determine if there are any minor or major deficiencies in the method. If there are minor deficiencies, such as the need to substitute one item for another, the EPA chemist will call the registrant to clarify those points. If there are major deficiencies, such as the entire cleanup procedure being left out, the EPA chemist will send comments to the technical reviewer in headquarters with a recommendation that the package be returned to the registrant. If the chemist determines that the registrant has submitted a complete method that meets all the requirements, it may be further evaluated in an EPA laboratory.

(iii) Priority for evaluating the methods will be determined by the needs of the Pesticide Program and the issues associated with pesticides undergoing registration and reregistration. The more detailed standard

evaluation procedure (SEP) that EPA plans to use to evaluate the written methods and the standard operating procedure (SOP) to be used in the laboratory evaluation have been developed and are available at the ECL at Bay St. Louis, MI. Please call 601–688–3253. **The effective data for the submission of soil and water methods, and performance data for those methods, is 12 months after the date of this guideline.** This includes soil and water methods sent to the Agency for registration and/or reregistration.

(3) **Format for reporting environmental chemistry methods.** The following format should be used in writing up the results of testing.

(i) *Title/Cover Page.*

(ii) *Certification.* (A) Certification of authenticity by the study director (including signature, typed name, title, affiliation, telephone number, and date, etc.)

(B) Statement of adherence to the FIFRA GLP.

(C) Statement of claims for nonconfidentiality, trade secrets, or proprietary data.

(iii) *Table of Contents.*

(iv) *Summary.* Provide a brief description of analytical procedures and instrumentation.

(v) *Materials.* (A) Equipment (list and describe).

(B) Reagents and standards (list and describe source and preparation, also MSDS sheets must be available for standards).

(C) Safety and Health (describe any special precautions that need to be taken with solvents or reagents and any procedural steps that require special precautions to avoid safety or health hazards).

(vi) *Methods* (A) Principles of the analytical methods.

(B) Analytical procedures (describe in a detailed stepwise fashion).

(*1*) Source and characterization of control samples, e.g., soil (textural class, pH, percent organic matter, etc.).

(*2*) Preparation of samples.

(*3*) Extraction (demonstrate efficiency in relevant soils).

(*4*) Fortification, if applicable (i.e. during method validation runs).

(*5*) Clean-up.

(*6*) Derivatization (if any).

(C) Instrumentation. (*1*) Description, e.g., make/model, type/specifity of detectors, columns (packing materials, size), carrier gases, etc.

(*2*) Operating conditions, e.g., flow rates, temperatures voltage, etc.

(*3*) Calibration procedures.

(D) Potential interferences—describe the effects of the following on signal enhancement, masking or suppression of signal and their impact on the test results:

(*1*) Sample matrices.

(*2*) Other pesticides.

(*3*) Solvents.

(*4*) Labware.

(E) Confirmatory techniques—describe confirmatory techniques, i.e. GC/MS, LC/MS, second column, etc.

(F) Time required for analysis—give the time required to take a sample/set completely through the analytical procedure, including sample preparation, extraction, cleanup, derivatization, and determination steps.

(G) Modifications or potential problems—describe any unique steps where little variation is allowed and any potential problems and/or modifications that were made to the analytical procedures.

(H) Methods of calculation—describe calculations in a step wise fashion and include calibration factors, calibration curves for parent compound, metabolites, and degradates, etc.

(I) Copies of chromatograms and/or spectra—representative sample should be submitted for each analyte measured in each matrix at all spiking levels, including method and matrix blanks. Copies of chromatograms and/or spectra are also required for the standards that were used to quantitate the analytes in the representative matrix submitted to EPA.

(J) Other—describe any and all additional information the registrant considers appropriate and relevant to provide a complete and thorough description of the soil and water method.

(vii) *Results/Discussion.* Describe expected performance of method.

(A) Method validation results and test levels.

(B) Accuracy (expected mean and range of recoveries).

(C) Precision.

(D) Limit of quantitation (provide definitions).

(E) Ruggedness testing, if performed.

(F) Discussion of selectivity and specificity of method (if applicable).

(G) Limitations.

(H) Independent laboratory validation (if available).

(viii) *Conclusions.* Discuss applicability of the soil and water method for measuring specific test compounds in various matrices, ranges, expected recoveries, interferences, etc.

(ix) *Tables/Figures.*

(x) *References.*

(g) **References.** The following references should be consulted for additional background material on this test guideline.

(1) Spencer, W.F. et al. Worker reentry into pesticide treated crops. II. Procedures for the determination of pesticide residues on the soil surface. *Bulletin of Environmental Contamination and Toxicology* 18:656–662 (1977). This paper contains a procedure for sampling of fine, dry particulate matter from the soil surface and a procedure for extraction of pesticide residues from soil.

(2) Berck, B. et al. Worker environment research: Rapid field method for estimation of organophosphorus insecticide residues on citrus foliage and in grove soil. *Journal of Agricultural and Food Chemistry* 29:209–216 (1981). The procedure for sampling fine surface soil material in this paper may be appropriate for damp soils as well as wet soils.

(3) Smith, C.A. and F.A. Gunther. Rapid estimation of organophosphorus pesticide residues in citrus grove soil. *Bulletin of Environmental Contamination and Toxicology* 19:571–577 (1978). This paper reports procedures for analysis in the field of pesticide residues sorbed to surface soil.

(4) ACS Committee on Environmental Improvement. Principles of Environmental Analysis. *Analytical Chemistry* 55:2210–2216 (1983).